

Pretreatment, Recycling, and Regeneration Strategies of Cathode Active Materials from Spent Lithium Ion Batteries

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Abstract

Lithium Ion Batteries (LIBs) have paved the way for the creation of portable consumer electronics and electric vehicles. The demands for LIBs of various chemistries show no sign of slowing. Many valuable metals, like Lithium and Cobalt, are contained in batteries, located primarily on the cathode component. The burden from increasing demand of LIBs has attracted attention to reuse the valuable active materials from the cathodes. This paper reviews the recent development of reusing spent LIBs in three categories: Pretreatment, Recycling and Regeneration. Pretreatment covers discharging, dismantling of the spent LIBs and separation of the useful part from waste; Recycling focuses on the recovery of value materials, four strategies (pyrometallurgy, hydrometallurgy, biometallurgy and electrochemical process) are discussed in details; Regeneration revives the spent electrodes, the mostly used methods are organized, including solid state synthesis, hydrothermal treatment, sol-gel and co-precipitation method. We summarize the advantages and disadvantages of each method, aim to organize the state-of-the-art technologies and provide a guideline for future development.

Keywords: Lithium ion battery • Valuable metal • Pretreatment • Recycling • Regeneration

Introduction

Rechargeable Lithium-Ion Batteries (LIBs) have revolutionized our world and facilitated the creation of portable computers, compact smart phones, digital cameras, and recently the electric cars. Battery demand is increasing exponentially stemming from declining price, advent of electric vehicles and increasing sales of consumer electronics. Just by looking at the electric vehicle market, 4 million electric cars were produced in 2020 globally and 12 million more are expected in 2025, this massive spike in demand will strain our ability to produce enough valuable metals, especially Li, Co, and Ni to meet this demand. In LIBs, 6-12 kg Co and 36-48 kg Ni are required per 100 kg cathode. From 2016 to 2018, the price of Co has been raised from \$22 to \$81 per kg, presenting clear evidence of short storage and rising demand of novel metals used in batteries. A consequence from such a fervent demand would be significant amount of LIB waste containing economically valuable materials like Li and Co, which are the targets of most recycling processes. Reusing batteries is not only economically sound, but also beneficial for the environment: LIBs in landfills can leach toxic chemicals into the soil. The treatment of spent LIBs also helps to reduce amount of materials going into a landfill since usable space is becoming limited.

Therefore, it has become a shared worldwide effort to find efficient and low-cost procedures to reuse spent LIBs [1].

A LIB comprises of cathode, anode, electrolyte, separator, current collectors and plastic/metal shells. Cathode materials are mostly lithium metal oxides such as LiCoO_2 (LCO), $\text{LiNi}_{1-x}\text{Co}_x\text{Mn}_{1-2x}\text{O}_2$ (NCM), LiMn_2O_4 (LMO) and LiFePO_4 (LFPO), containing valuable elements for recycling; Anode materials including graphite, Si, TiO_2 and alloys could be partially reused; electrolyte (consisting of Li salt with organic solvents), separator (typically a single layer or multi-layer of polyethylene or polypropylene), and plastic shell are simply waste; current collectors (Al and Cu) could be recycled. The working process of a LIB is its charging /discharging process, accompanied by Li^+ intercalation and de-intercalation. Solid electrolyte interface (SEI), Li dendrite and complicated Li compounds are formed, some of them could react reversibly, releasing Li^+ ; others can't, consuming active Li^+ and degrading the performances. A LIB's lifetime is typically ~2 or 3 years after 200 to 300 charge/discharge cycles when the capacity fades to 80% of the rated battery capacity. After that, a LIB is treated as "spent" or "used". Spent LIBs usually contain 5-7 wt.% Li, 5-10 wt.% Co, 5%-20 wt.% Ni, 5-10 wt.% other metals (Cu, Al, Fe, etc.), 15 wt.% organic compounds, and 7 wt.% plastic. Some are valuable and

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some are trash. How to reuse the spent LIBs in a sufficient and economic way is the main focus of this review.

Hereby, we systematically reviewed the papers published for reusing the spent LIBs and categorized them into three strategies of pretreatment, recycling and regeneration. The pretreatment is the work necessary prior to getting the valuable materials, including discharging, dismantling and separation of useful materials from waste; Recycling is to extract the valuable materials from the cathode of spent LIBs after pretreatment: pyrometallurgy, hydrometallurgy, biometallurgy and electrochemical process, the four mostly used methods are organized here; Regeneration is to revive the spent cathode by adding Li salt to compensate Li loss and by thermal treatment to recover the structure: solid state synthesis, hydrothermal treatment, sol-gel and co-precipitation as the main regeneration methods are discussed in details. We also summarize the advantage and disadvantage of each strategy and method, hoping to provide a clear view of the state of art treatment of spent LIBs and useful information for the people interested in this area.

Pretreatment

The ultimate goal of pretreatment is to separate as much as possible the components of the battery, so these materials do not interfere with the leaching of the materials of interest, in the scope of this paper, is the cathode active materials. As seen in Figure 1, pretreatment can be simplified into 3 steps: discharge, dismantling, and separation. The pretreatment processes can also be divided into lab-scale and industrial scale categories, which is an important distinction. The following will be a detailed discussion of individual step in pretreatment and research progress in alternative processes with aims at sustainability and improving leaching efficiencies.

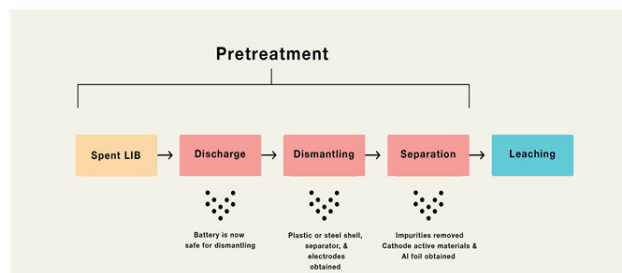


Figure 1. General schematic of the pretreatment process before leaching.

Discharge

Before dismantling, it is important the battery be discharged to prevent short-circuiting and self-ignition of battery rolls if anodes and cathodes touch. Discharge is done by soaking the spent LIB in a salt

solution, with NaCl being the most popular, Na_2SO_4 is also common, but leaching efficiency has been shown not to be as effective as NaCl. The level of discharge must be kept in mind because at complete discharge, copper can diffuse into the electrolyte and affect leaching efficiency, the exact level of discharge that is optimal has not yet been determined. If NaCl is chosen as the salt, determined that a 10 wt.% solution was optimal with the lowest amount of volatile organic compounds released into the leachate, and the highest amount of valuable metals leached into the liquor to recycle

note, discharge is different for electric vehicles because salt solutions are not suitable for high voltage cells. There is an alternative for the discharge of vehicle batteries by direct ohmic discharge of the battery through a load-bearing circuit.

Dismantling

There are three possible mechanisms for dismantling: (1) manual, (2) semi-automatic, and (3) fully-automatic. It is imperative that all steps were carried out using safety glasses, gloves, and gas masks. Manual dismantling is typically unscrewing or loosening components of the battery, usually with use of a pneumatic tool. During dismantling, the anode and cathode should be separated because the goal is to extract the active materials from the cathode. A procedure of only manual dismantling may work for lab-scale purposes, but is cost-prohibitive at the industrial scale, where automation is employed to some level [2].

During dismantling, toxic products can be produced that must be taken into consideration. Metals like Co and Ni are toxic to human health, especially as a respiratory hazard. Electrolytes can produce many toxic compounds like fluorophosphate, fluoroethanol, hydrogen fluoride, and fluoroethylene. Removing electrolyte before shredding can prevent the toxic products from forming. The electrolyte is typically evaporated by heating, the emitted gases pollute the environments.

Obviously, the dismantling of batteries from electric vehicles is a wholly different procedure. At present, there is no standardization of design for battery packs, modules, or cells within the automotive sector. Due to manufacturers having many different designs of their battery packs, thus writing a disassembly strategy as one size fits all is difficult. The retrieved battery can have sealants in the module, adhesives sticking cells together, and soldered components that make disassembly difficult. Manual disassembly of car batteries can be time-consuming and economically infeasible when a large number of spent batteries need to be recycled, and in industry automation at some level has been the norm. In Germany, the minister of the environment has invested 13 million euros in a robotic battery dismantling project with groups consisting of the Fraunhofer Institute, the Karlsruhe Institute for Technology, Cluasthal Environmental Technology Research Centre, and DeMoBat. Car batteries are not the only batteries that automated disassembly have been applied towards. There have been strategies to automatically dismantle phone batteries in the works. Apple's open material recovery lab has developed robots to disassemble different iPhone models at a rate of 200 phones per hour.

As an alternative to dismantling, crushing and shredding the battery have been employed to simplify the process. Also, shredding or crushing the battery in an inert atmosphere has been used in industry to combine the discharging step and dismantling step to make the process cheaper as well. There are dangers associated with crushing and shredding the battery, such as fire and emission of toxic gases. Freezing by liquid nitrogen could be used to reduce the chances of fires from short-circuiting or overheating from shredding. The crushing and shredding approach can obviously be applied in the lab setting as well. A two-stage crushing procedure combined with a sieving/magnetic separation process before recovery. After discharging and crushing, used wind sieving to remove the separator,

NaOH to dissolve the Al, supercritical CO₂ to extract the electrolyte, and finally used oscillation sieving to retrieve the copper collectors.

Separation

With the cathode isolated during dismantling, it is imperative to eliminate impurities from the cathode, such as Cu, Al, Fe, and carbon, to obtain the valuable cathode material for the subsequent leaching step. The active cathode materials (usually lithium oxides) must be separated from the other cathode materials (conductor, binder, and current collector) to achieve high recycling efficiency. Thermal and chemical separations are the two prominent ways to achieve this. Besides, another pretreatment separation strategy termed mechanochemical will be discussed further, which has been employed to increase the leaching efficiency of cathode active materials.

Thermal separation: PVDF is the most common binder in LIBs because of its thermochemical stability and mechanical strength. These strengths of PVDF are detrimental for recycling because it makes the separation between aluminum foil and cathode materials difficult. PVDF, if not completely removed in pretreatment, can affect the efficiency of the leaching step. One strategy to removed PVDF is through thermal pretreatment. The advantages of thermal pretreatment are the simplicity and scalability of the process. To note, thermal treatment is able to remove the carbon content from the cathode, and this improves the leaching efficiency for lithium due to carbon acting as an adsorbent for lithium. According to literatures, thermal pretreatment conditions can be in the range of 350–700°C and the treating time vary widely as well. The optimal temperature for thermal pretreatment was found to be 500°C for 15 min for liberation efficiency by Zhang's group. Adjustments to the thermal process can be made to mitigate the production of harmful gases. For example, CaO as a reaction medium that allowed the PVDF in the cathode electrode to be decomposed at a lower temperature of 300°C, which resulted in no toxic HF emission.

Some negatives of the thermal pretreatment are the high energy cost, device investment, and toxic gas emissions. An alternative is the pyrolysis of cathode material under vacuum. Vacuum pyrolysis lowers the decomposition temperature of the organic compounds, thus preventing the release of toxic gases, protecting copper and aluminum from being oxidized, allowing for recycling and the separation of valuable metals to be achieved without scraping or sieving. Introduced a novel low-temperature pretreatment method called cryogenic grinding, allowing for the collection of Al, which is often destroyed by oxidation in many recycling processes. Low temperatures weaken the PVDF binder, as well as assisting Al separation from cathode material by improving the mechanical properties of Al, which allowed to resist grinding, thus improving separation by sieving [3].

Chemical separation: The use of organic agents is another popular method of removing the binder. The most common procedure is using N-Methylpyrrolidone (NMP) or Dimethylformamide (DMF) as the solvent for 1 h, either under heating or ultrasonication. Acetone and Dimethyl Sulfoxide (DMSO) are also used, but they volatilize easily versus solvents like NMP and DMF. Dimethylacetamide (DMAC) was better at separating the active cathode materials from aluminum compared to NMP, DMF, DMSO and acetone; the separation was able to be completed at a lower temperature of 30°C

and time of 30 min. Interestingly, citric fruit juice was used as a novel, green solvent to remove the PVDF binder that avoided the generation of toxic HF. Some negatives to consider are that solvent dissolution methods can be high cost and produce toxic products, especially at the industrial scale. It is possible to combine solvents with thermal pretreatment to maximize separation. The cathode scraps with NMP at 100°C for 1 h to separate cathodic active material. The recovery of copper and aluminum in their metallic form was achieved. After drying at 60°C for 24 h, the cathode was calcined at 700°C for 5 h in a muffle furnace to remove the remaining carbon and PVDF.

It is possible to dissolve the aluminum using a base like NaOH, and using thermal pretreatment to burn off the PVDF residues from the cathode active materials. Using NaOH can prevent LiPF₆ from hydrolyzing and producing toxic gas. The cathode scraps into small pieces and dissolved with NaOH solution at room temperature for a few hrs. After the complete dissolution of Al-foil, the powder was collected by filtration and heated at 700°C for 2 h to burn off the organics. An exhaust gas recovery unit is used to manage hazardous gases during the calcination process. The obtained powder was then ground for 30 min to obtain smaller particles with a higher surface to enhance the leaching efficiency.

Mechanochemical separation: The mechanochemical pretreatment combines the effects of mechanical grinding and adding of co-grinding agent to improve the recovery of cathode active materials, such as Li and Co. The method could avoid the use of strong acids or bases, thus making the procedure more environmentally friendly and safer. For example, when lithium oxides were grinded along with co-grinding agents like EDTA or PVC, the grinding could decrease the particle size, and the co-grinding agents would break and deform the crystal structures, ultimately generating products with decreased activation energy, thus improving the reactivity for leaching. Without the co-grinding agents, as found the leaching efficiency decreased significantly. As discovered by the recovery rates of Co and Li could increase with longer grinding time, with the optimal grinding time being 4 h, when considering the negligible increase of recovery rate and increased energy consumption past 4 h. Besides EDTA or PVC, other co-grinding agents can be used: Iron powder with purity of 98% to the LiCoO₂, producing a powder with much enhanced leaching efficiency. Compared to the sample without adding iron powder, the leaching efficiency increased from 23% to 80% for Co and from 39% to 63% for Li.

The mechanochemical pretreatment could promote the regeneration process of NCM cathodes, evident in experiments done. The cathode powder was ball-milled in combination with LiCO₃. Afterwards, Sintering was performed at the optimal temperature of 800°C to obtain the regenerated NCM cathode. According to the characterization results, the mechanochemical samples had better layered structure compared to samples that did not undergo mechanochemical pretreatment. The mechanochemical activated sample also had a better battery performance than the untreated sample, exemplified by a regenerated NCM with a discharge capacity of 133 mAh/g after 100 cycles and a capacity retention of 80.7%. The mechanochemical treatment may improve the diffusions of Li⁺ from added LiCO₃ and nickel ions from the spent NCM powder, decreasing the cationic disordering, resulting in an improved layer structure. Although, the convenience of the mechanochemical

methods described is attractive, the long reaction time and high energy consumption make it difficult to scale up to the industry level.

Recycling Strategy

The recycling strategy is the significant part of the whole recovery process, focusing on the extraction of valuable metals from spent cathodes in their alloy form or solution state. Based on the overall costs and environmental impacts, several approaches have been developed for different chemistries of the most common LIB cathodes, such as LiCoO_2 , LiMn_2O_4 , $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$, and LiFePO_4 . As shown in Figure 2, these recycling methods can be categorized into pyrometallurgical, hydrometallurgical, biometallurgical and electrochemical recovery.

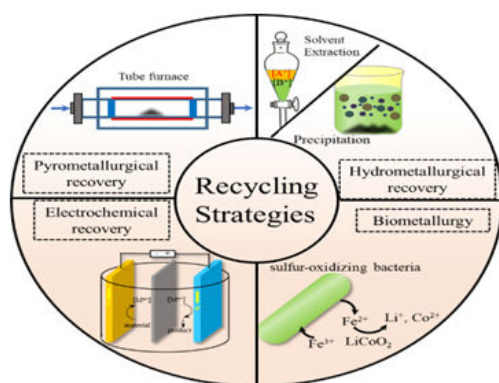


Figure 2. Illustration of recycling strategies for spent LIBs.

Pyrometallurgical recovery

The traditional pyrometallurgical recovery reduces the spent LIBs through a high temperature process to obtain alloys of Co, Ni, and Mn. No pretreatment is required and spent LIBs could be fed directly to a furnace. The graphite, organic solvents, plastics and even binders in the batteries provide heat during combustion. This is a rough method, high energy consumptions together with air pollutions are the lethal defects. Another negative is that lithium and other valuable metals can't be recovered directly under this process, the as formed slags need further separations. However, due to its simplicity and high productivity, this method is widely used for large scale recycling of spent LIBs currently by many big companies, such as Umicore and Accurec. For research, pyrometallurgical recovery is expected to proceed at a low temperature without hazardous gas emission. It has been reported that Li compounds (such as Li_2CO_3 and Li_2O) suffer from severe volatilization at temperature above 750°C , significantly reducing the recycling efficiency. Thus, low temperature pyrometallurgical recycling is becoming a research hotspot, which includes reduction roasting and salt roasting, a process flow chart is shown in Figure 3.

Reduction roasting refers to extract target metals by reduction reaction under vacuum or inert atmosphere. For instance, developed a novel process of carbothermic reduction of LIB materials: 20% graphite was added as the reductant together with 10% NaOH as the catalyst, the recovery happened at 520°C for 3 h, slags with Li_2O and CoO were obtained from spent LiCoO_2 . Further leaching with deionized water could achieve Li recovery efficiency higher than

93%, while CoO remained in slags, making downstream separation easy. The same procedure was applied to recover the valuable metals from spent NCM cathodes, where graphite from waste anode was used as reductant directly [4].

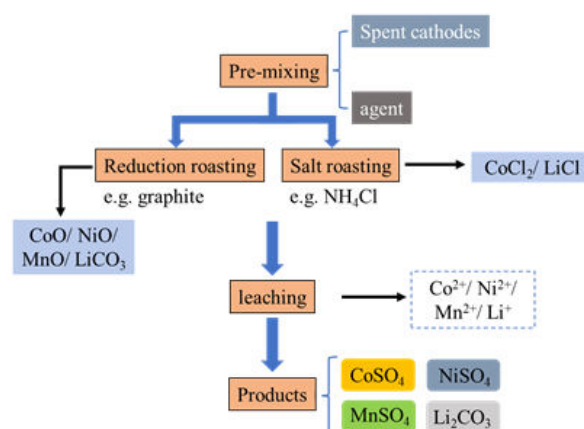


Figure 3. The process flow chart of the overall recycling of spent LIBs.

Salt roasting could reduce the calcination temperature and increase the recovery rate by adding salt co-solvents, including sulfate roasting, chlorination roasting, and soda roasting. Its main principle is to convert the cathode materials into water soluble salts by the action of co-solvents. For example, an ammonium chloride roasting approach to achieve water-soluble LiCl and CoCl_2 from LCO at 300°C , the recovered salts were used to regenerate LiCoO_2 , which showed an initial discharge capacity of 139.8 mAh g^{-1} at 0.5 C with a retention rate of 99% after 100 cycles. The reduction roasting and salt roasting could reduce the calcination temperature significantly, make the further separation easy and suppress the hazardous gas emission to a certain level. However, adding reductants and salts make the recycling more complicated, the corresponding costs could rise. How to scale up from lab research to industrial application at a reasonable cost is the challenge.

Hydrometallurgical recovery

Hydrometallurgical method is using aqueous solutions to leach the required metals, it possesses the positive characteristics of high recovery efficiency, high metal selectivity with limited gas emission. Hydrometallurgy has even greater potential for sustainability than pyrometallurgy in the recycling of spent LIBs. However, complicated steps lead to a longer route and wastewater is produced during process. Many studies focusing on type and concentration of leachate, leaching time, solution temperature, solid to liquid ratio and reductants have been conducted to obtain the final products. The key steps of this process are leaching and purification. Leaching of LIBs is the dissolution of target active materials from the solid state into solution by leaching reagents, and purification including solvent extraction and chemical precipitation is used to separate metal ions or remove impurities.

Leaching: There are several categories of leaching reagents such as inorganic acids, organic acids, and alkali bases. Inorganic acids like HCl , HNO_3 , H_2SO_4 and H_3PO_4 , are popular due to the high capacity of dissolving metals. The H_3PO_4 as a leaching and

precipitation agent for recovery of the spent LiBs, phosphate precipitation was directly obtained, Co recovery was over 90% with high purity. The leaching efficiencies of HCl, HNO₃, and H₂SO₄ for Co and Ni under the same conditions, concluded that HCl had the highest leaching efficiency. However, the issue with inorganic acids was the consequence of toxic gas emissions, which complicated the process and harmed individuals. Thus, the research for green organic acids manifests. Naturally degradable malonic acid (also called carotene acid) as a leaching agent, the leaching efficiencies of Li, Ni, Co, and Mn were over 95%, and the whole process is mild.⁸³ Frequently used organic acids are citric acid, oxalic acid, and acetic acid.

To accelerate the leaching process, a reductant agent is sometimes used to adjust the valence of metal ions to a more soluble state. The reductant agent, even if it does not increase recovery efficiency, will result in a less leachate needed, which was demonstrated by oxalic acid experiment. The most common

reductant is hydrogen peroxide (H₂O₂), Stusulfite and glucose were also reported as efficient reducing agents. Employed acetic acid as the acid species and H₂O₂ as the reductant to achieve a 99% recovery of Mn, Co, and Ni. The optimal parameters of leaching using organic acids are summarized in Table 1.

Acid	T (°C)	Time (min)	Concentration (M)	Reductant (vol%)	S:L (g/L)	Efficiency (%)
Acetic	60	10	6	H ₂ O ₂ (4)	33	98% for NMC
Aspartic	90	120	1.5	H ₂ O ₂ (4)	10	60% of Li and Co
Citric	60	120	2	H ₂ O ₂ (1.25)	30	93% Li, 82% Co
Malic	80	180	1.5	grape seed (5 g/g)	20	99% Li, 92% Co
Oxalic	100	n/a	0.23	H ₂ O ₂ (3.6)	15	97% Li and Co

Table 1. A comparison of the optimal conditions of organic acids for leaching.

Alkali leaching was developed in pursuit of high leaching efficiency. Ammonia has a high selectivity towards forming complexes easily with Co, Li, Ni, and Cu, while hardly with Fe, Al, and Mn. Spent LIBs in ammonia and ammonia carbonate, which formed a relatively stable buffer system to metal-ammonia complexes, ammonia sulfite was then added as the reductant, the recovery was over 90.16% for cobalt. Xu's group developed a method of using waste Al foil as the in situ reductant and then applied NaOH solution to leach Li and Co with a leaching efficiency of 93.67% and 95.59%, respectively.

Purification: Purification is a downstream process to obtain pure compounds from the mixture, it is the very important part of battery recycling. Purification mainly includes solvent extraction and chemical precipitation: 1) Solvent extraction is the process of using organic and aqueous phase system to separate target metal ions by different relative solubility of compounds in the two phases. The distribution coefficient (D) and separation factor (SF) are used to determine the extraction yield and phase separation performance, reflecting the efficiency of solvent extraction. The distribution

coefficient (D) is the ratio of the metal ion concentration in two phases at equilibrium, and its value shows extraction yield of metal ions; the Separation Factor (SF) is calculated as the ratio of two different metal ion distribution coefficients, $SF = D_A/D_B$, its value indicates the separation performance. Following the rule: $SF > 10$ = possible separation, $SF > 100$ = good separation, and $SF > 1000$ = excellent separation. During the extraction process, several factors affect the efficiency, including the extraction system, extractant concentration, organic/aqueous (O/A) ratio, pH, temperature and time as shown in Figure 4.

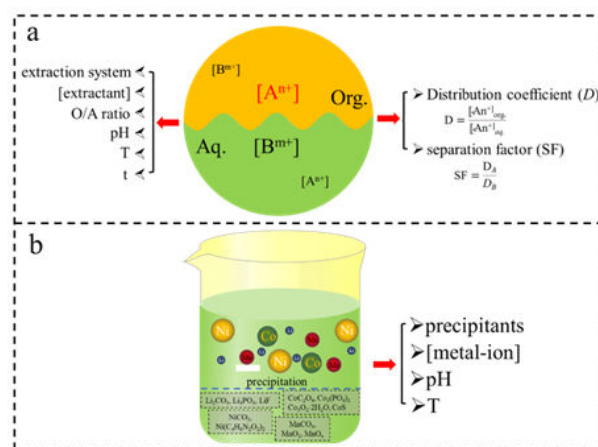


Figure 4. Illustration of the solvent extraction and chemical precipitation in separation.

Chemical precipitation is widely applied to separate metal ions from complex systems, the efficiency relies on the different solubility of metal compounds in certain solutions. pH plays an essential role for the precipitation. Generally, the impurity cations like Fe³⁺, Al³⁺, and Cu²⁺, precipitate at relatively low pH (Figure 5a), while most target metal ions such as Co²⁺, Ni²⁺, and Mn²⁺, precipitate at high pH (Figure 5b). Thus, by adding precipitant and adjusting pH, the first step is to precipitate and separate impurities, then followed by the precipitation of transition metal ions, finally Li⁺ will be the only one in the solution for recovery. Again, type of precipitant and its concentration, pH and temperature are the main factors to be considered.

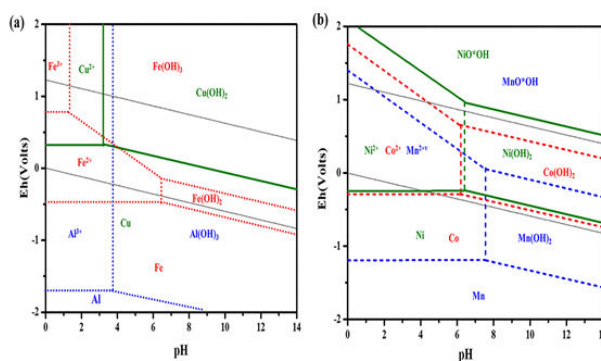


Figure 5. (a) Eh-pH diagram for the Al-H₂O, Cu-H₂O, and Fe-H₂O systems (25°C, [Al]=[Cu]=[Fe]=0.2 mol L⁻¹); (b) Eh-pH diagram for the Ni-H₂O, Co-H₂O and Mn-H₂O systems (25°C, [Ni]=[Co]=[Mn]=0.2 mol L⁻¹). Eh represents the oxidation-reduction potential vs. SHE (standard hydrogen electrode).

Solvent extraction and chemical precipitation as the main purification methods in recycling of spent LIBS are reviewed here, there still remain lots of other purifications which are beyond the scope of this review. Due to the complexity of the real world, the methods don't stand alone, instead they often combine together to achieve higher efficiency with lower cost than the sole counterpart. For example combined multiple separations, developing leaching-cascade extraction-precipitation process to recover spent $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$. The recovery efficiency/purity were 96.15%/ 100% for Li, 91.54%/98% for Ni, 91.15%/93% for Co and 91.56%/ 100% for Mn.

Biometallurgy

Biometallurgy (also called bioleaching) utilizes microorganisms and their chemical products to solubilize metals at mild conditions with little energy consumption, it is an eco-friendly technology. Bacteria and fungi are the most common bioleaching organisms used. For example, *Aspergillus Niger* was evaluated and shown high recovery of Cu and Li, but low recovery of Co. However, Biometallurgy suffers from slow kinetics, long processing time, low recovery efficiency and cultivation of microorganisms. Biometallurgical recycling could be complemented by hydrometallurgical and pyrometallurgical processes. An efficient way of combining biometallurgy with hydrometallurgical leaching to recover Co, Li and Mn, the results showed high recoveries of 91.45%, 93.64% and 87.92% for Co, Li and Mn, respectively. By now, there is no consensus on the bioleaching mechanism of LIBs. The generally accepted mechanism is the indirect mechanism, where bacteria generated metal sulfide-oxidizing intermediate, rather than a direct electron transfer from the metal compounds to the cell. The reported studies of biometallurgy are relatively small, leaving large spaces for future research in this field.

Electrochemical recovery

Compared with pyrometallurgy and hydrometallurgy, the electrochemical method could achieve high recovery efficiency without producing any impurity. When a potential is provided by the external energy source and applied to the two electrodes of the electrolyser, a redox reaction of ions in the leaching solution was induced, which resulted in the reduction of metal ions to metal on the cathodes. The factors of recovery efficiency include pH, electrode materials, applied current density and voltage. There are numerous examples of electrochemical approaches: Achieved high efficiency of 96.9% at pH of 5.4 with a potential of -1.00 V and a charge density of 10.0 A cm^{-2} ; established a new process to recover and regenerate LCO on nickel plate at constant current density of 1 mA cm^{-2} ; used the electrodialysis method to separate Li^+ with a cation-exchange membrane, dissolved Li_3PO_4 was the anode electrolyte (anolyte) and subsequently Li_2CO_3 was obtained using a precipitation process as shown in Figure 6a.

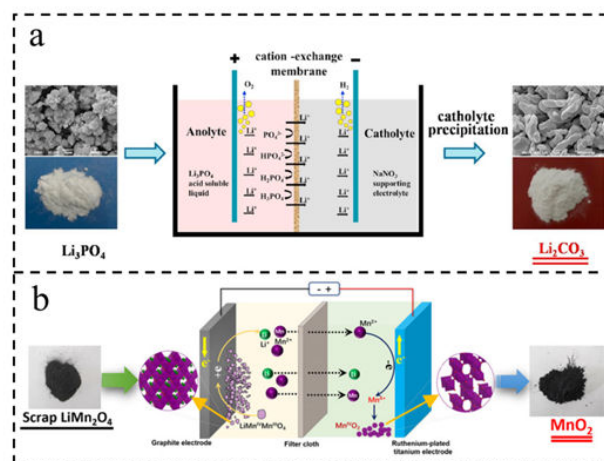


Figure 6. a) The electrodialysis process for recovery of lithium; b) slurry electrolysis for recovery of manganese.

A recovery strategy for Li and regenerated NCM from spent cathode materials by electrochemical leaching. During this process, more than 98% leaching efficiency of Li was achieved from solid compounds into electrolyte by applying an potential of 32 V, the process was similar to the Li^+ de-intercalation during the charge of a LIB, subsequently the cathode material was separated from Al foil and then recovered with 98.5% efficiency. A slurry electrolysis (Figure

6b) process to recycle Li and Mn from scrap LiMn_2O_4 without reagent consumption. The whole process was environment friendly, more than 99% of Li and 92% of Mn were leached from LiMn_2O_4 at 363 K in cathode chamber and subsequently MnO_2 was precipitated in the anode chamber after oxidizing Mn^{2+} to Mn^{4+} .

The comparisons of the four recovery methods are organized in Table 2, it is not a surprise that each method has its advantages and disadvantages. How to combine the advantages and find a sufficient and general way with low cost for large scale recycling is still the hot spot of research, which may require the efforts of several generations.

Recovery method	Advantages	Disadvantages
Pyrometallurgical recovery	simplicity, productivity, fast rate and easy pretreatment	high energy consumption, emission of hazardous gases, slags need further separation
Hydrometallurgical recovery	high recovery efficiency, high metal selectivity with limited gas emission	consumption of acid/alkaline solution, complex operation steps, and wastewater production
Biometallurgical recovery	mild conditions with little energy consumption, eco-friendly technology	slow kinetics, long processing time, low recovery efficiency and cultivation of microorganisms.
Electrochemical recovery	high recovery efficiency without producing any impurity	water splitting occurring at high potential, low electricity conversion efficiency

Table 2. Comparisons of four recovery methods.

Regeneration

Regeneration is a strategy to revive the spent cathode directly instead of extracting value elements. Since traditional recycling processes involve multiple complicated steps such as separations of different valuable metals from used active materials and re-synthesis of new cathode, this simple and low-cost approach has great potential for the recovery of spent LIBs. The novel concept is the regeneration of electrode materials by directly converting spent electrode to new electrode without intermediate separation. The direct regeneration strategy offers several advantages: 1) avoid the separation of multiple metal ions; 2) reduce the toxic gas emissions; 3) improve the utilization rate of metal ions by avoiding the loss of valuable metal elements; 4) eliminate the steps of re-synthesizing electrodes and tedious chemical analysis, save time and costs, and improve recycling efficiency. In general, the primary regeneration includes [5].

Solid-state synthesis

The solid-state synthesis method has been broadly used to regenerate cathode materials from spent LIBs. Briefly, the active cathode materials separated from current collectors are mixed with Li sources at an appropriate ratio and then heat-treated at a certain temperature to compensate the Li loss from the spent LIBs. This method has been used for regeneration of LiCoO₂, LiNi_xCo_yMn_zO₂ and LiFePO₄ materials. A green and efficient solid-state process to regenerate spent LiCoO₂ materials. In their study, LiCoO₂ was regenerated by mixing with Li₂CO₃ using a solid state synthesis with a calcination temperature range of 850-950°C. The regenerated LiCoO₂ had similar morphology and particle sizes as those of commercial LiCoO₂. Compared with the fresh LiCoO₂, the sample regenerated at 900°C even had a better layered structure, more suitable size distribution, higher tap density, and lower specific surface areas, which satisfied commercial requirements. The results proved that the calcination temperature was a key factor allowing the regenerated cathode to achieve high electrochemical performance. For the electrochemical properties, the initial discharge capacity of the sample calcined at 900°C could reach 152.4 mAh g⁻¹ similar to the fresh commercial LiCoO₂ (140-155 mAh g⁻¹). The LiCoO₂ regeneration mechanism was unveiled. By adding Li₂CO₃, during the process of solid-state synthesis, the following reactions happened.

LiFePO₄ cathodes could also be regenerated through a solid-state process. Li et al. mixed scrapped LiFePO₄ electrode with Li₂CO₃ and regenerated it at 600°C to 800°C for 1 h. The results showed that impurities like FePO₄ and P₂O₅ reacted with Li₂CO₃ to reform LiFePO₄, residual PVDF binder gradually decomposed as the regeneration temperature increased, decreased agglomeration resulted in improved electrochemical performances. However, when the regeneration temperature increased to 700°C, the impurities appeared again due to the decomposition of LiFePO₄, which caused the inferior battery performances. Among all the regenerated LiFePO₄ cathodes, the one regenerated at 650°C had the best cycle and rate performance.

The solid-state synthesis is a simple and eco-friendly method to regenerate the cathode from spent batteries, the results have proved its potential for large scale industrial applications. However, the main challenge is that some impurities are hard to remove completely from

the cathode materials. For example, the LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ cathode recovered by solid-state synthesis could not reach the high capacity of commercial counterpart due to the presence of impurities like LiF and Li₂CO₃. Besides, the Li compensation level, the optimal calcination temperature and time are material and even sample dependent, all these problems hinder the commercialization of solid-state synthesis method and require more attentions from the battery community.

Hydrothermal treatment

Hydrothermal treatment method is widely employed to regenerate cathode materials from spent LIBs. By mixing spent cathode materials with lithium-contained solution such as Lithium Hydroxide (LiOH) under certain temperatures, the cathode materials can be regenerated. Many small particles appeared on the surface of the renovated LiCoO₂, reflecting a morphology evolution of the regenerated LiCoO₂. The presence of these particles proved the regeneration of LiCoO₂ by hydrothermal treatment was based on 'dissolution-precipitation' mechanism.

The hydrothermal treatment

with simple thermal annealing to regenerate LiCoO₂ and investigated the electrochemical performances, in which LiOH solution was used as Li sources. During the hydrothermal step, the following reaction will occur. The electrochemical performances of the regenerated LiCoO₂ samples varied with treating temperatures. Among all samples, the one annealed at 800°C after hydrothermal treatment at 180°C showed the highest initial discharging capacity of 148.2 mA h g⁻¹ and remained 135.1 mA h g⁻¹ after 100 cycles at 1C. Furthermore, a mixed solution containing 1 M LiOH and 1.5 M Li₂SO₄ was used to replace the pure LiOH solution, the results demonstrated that LiCoO₂ treated with the mixed Li solution had the similar cycling and rate performance as the one treated with pure LiOH solution. Using mixed

Li salt solution as Li sources are effective in LiCoO₂ regeneration process via hydrothermal treatment, which provides more possibilities and can help reduce the operation cost.

Followed the same route, adopted hydrothermal treatment method to regenerate the NCM cathodes and investigated their electrochemical performances. NCM is a layered structure cathode and the capacity degradation is mainly due to the changes of crystal structure and microphase on the particle surface. Therefore, solving the problem of compositional and structural defects is the main focus when regenerating the NCM cathodes. The degraded NCM particles had the coexistence of layered, spinel, and rock salt phases, by applying hydrothermal treatment with annealing, the undesired spinel and rock phases transformed back to the pure layered phase which was identical to the pristine sample. The testing results proved that the electrochemical activities of the spent NCM cathodes could be fully recovered with high discharge capacity and good cycling stability by hydrothermal treatment. Hydrothermal treatment method can fix the degraded particles and maintain the primary morphology and structure of the cathode materials, resulting in the good electrochemical performances, other results also certified that high quality cathodes could be obtained by the hydrothermal reaction. The low energy consumption is another advantage. Therefore, this method has been widely applied to regenerate LiCoO₂ and NCM electrodes. However, the hydrothermal treatment method requires strict experiment conditions, it was also reported that high oxygen partial pressure was needed for NCM regeneration using this method.

Sol-gel method

To meet the requirements of reusing cathode material at industrial level, the cost and rate should be accounted during the regeneration. The sol-gel method is one of the most effective and economical processes. In a sol-gel regeneration process, acid leaching is required to convert metal ions to high valence state in the acid solution. Chelating agent will be used to induce hydrolytic and polymerization reaction to form sol. The cathode materials can be regenerated after drying and heated at a certain temperature to remove the organics. For example, a recycling route based on sol-gel method to regenerate NCM cathode materials. The process of regenerating the cathode materials consisted of several steps: (1) the cathode scraps were leached by lactic acid solution; (2) the molar ratios of Li^+ , Ni^{2+} , Co^{2+} , and Mn^{2+} were adjusted by adding their corresponding precursors; (3) $\text{NH}_3\cdot\text{H}_2\text{O}$ solution was added to adjust the pH value and the solution was heated at 80°C to form transparent sol; (4) The obtained gel was dried at 100°C and heated at 450°C to remove the organic contents. The NCM cathode regenerated by sol-gel method could obtain similar crystal structure, morphology, and electrochemical properties as the freshly synthesized NCM. The cathodes regenerated by sol-gel method could exhibit the similar morphology and electrochemical properties as the fresh materials. However, the sol-gel method involves complex procedures, which may increase the operation cost and energy consumption. Moreover, the acid leaching step required in the process could create additional harmful waste.

Co-precipitation method

Co-precipitation method has been developed to regenerate spent cathode materials. In a co-precipitation process, the impurities can be removed through precipitation after adding a precipitant and then cathode precursor can be obtained, the regenerated cathode is produced by mixing cathode precursor with Li sources, followed by calcination. Combined oxalic acid co-precipitation, hydrothermal and calcination processes to regenerate Li-rich layered $\text{Li}_{1.2}\text{Co}_{0.13}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{O}_2$ cathode materials. The physical, chemical and electrochemical properties of regenerated and fresh cathode materials were compared systematically. The regenerated cathode displayed smooth surface with well-distributed particles, excellent electrochemical performances with initial discharging capacity of 258.8 mAh g^{-1} at 0.1C . The cycle performance and rate capability of the regenerated $\text{Li}_{1.2}\text{Co}_{0.13}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{O}_2$ were almost as outstanding as the freshly synthesized one. This study indicated that regenerated cathode with homogeneously layered structure could restore the electrochemical performance of spent cathodes. The mixed type spent cathodes were leached by the solution of $4\text{M H}_2\text{SO}_4$ and $4\% \text{H}_2\text{O}_2$ and the impurities like aluminum, copper and iron were removed by precipitation and solvent extraction. Manganese sulfate heptahydrate, cobalt sulfate heptahydrate and nickel sulfate hexahydrate were used to adjust the ratio of Mn^{2+} : Co^{2+} : Ni^{2+} in solutions. The co-precipitation was completed by mixing the solution containing Ni, Co and Mn ions with NaOH and NH_4OH . $\text{Li}_2\text{MnO}_3\cdot 0.8\text{LiNi}_1/3\text{Co}_1/3\text{Mn}_1/3\text{O}_2$ was obtained by mixing precipitates with excess Li salts, followed by calcination. The regenerated cathode exhibited very high discharge capacities of $240\text{--}250\text{ mAh g}^{-1}$. Different metals of the cathode materials can be co-precipitated to form the precursors. This method is effective to regenerate different cathode materials with good electrochemical

properties. Also, the recovery efficiencies of Ni^{2+} , Mn^{2+} , Co^{2+} are normally over 90%. However, co-precipitation method consists several steps such as acid leaching and precipitation, making this method complicated with high cost.

Conclusion

With the ever growing automotive industry and the demand of consumer electronics remain as high as ever. The growing waste produced by spent LIB is worrisome and the cost of many valuable metals contained in the cathode is an economic incentive worth pursuing. In the paper, we systematically reviewed the recent technologies dealing with spent LIBs and categorize them into pretreatment, recycling and regeneration. Pretreatment is the first but important and complicated step for reusing spent LIBs, it is related to safety, environment, energy and recovery efficiency, which is often vaguely described in current literatures. In some traditional processes like pyrometallurgy, pretreatment is skipped with Li and Al lost in slag. Cutting off pretreatment introduces large amount of hazardous gas emission, impacting environment negatively. Many modern processes have been developed with pretreatment in mind to alleviate the aforementioned downsides. Pretreatment can be divided into discharge, dismantling and separation. Discharging is universally done first due to the safety issues, but methods can differ greatly from lab scale to industrial applications. Dismantling is to isolate valuable cathode from other parts (mostly waste) of spent LIBs, such as plastic shells, electrolyte, separator and anode. Separation is to eliminate impurities of the cathode materials like binder (PVDF), current collectors (Al) and additives (conducting carbon and others). Thorough pretreatment, we can maximize the recovery of valuable metals and minimize the negative effects to environment. However, the lengthy operation plus high energy consumption are the main drawbacks, cost should be put into consideration when a feasible pretreatment route is designed.

Recycling the valuable materials from the spent LIBs is the main purpose of most waste battery treatment, which includes pyrometallurgical, hydrometallurgical, biometallurgical and electrochemical recovery. The traditional pyrometallurgy is the high temperature treatment, skipping pretreatment and consuming lots of energy, low temperature pyrometallurgy including reduction roasting and salt roasting is the current research direction; hydrometallurgy is extracting valuable elements in aqueous solution, which could happen at room temperature with high recovery efficiency, however, the process is complicated involving multi-steps and affected by many factors as discussed in the paper; electrochemical recovery is based on the reduction of metal ions in electrolyzer by applying an appropriate potential, high recovery efficiency with high purity could be achieved, however, the parasitic reaction such as water electrolysis increases the energy consumption; biometallurgy uses microorganisms to solubilize metals, a green method with little energy consumption, the extremely slow kinetics prevents its large scale applications. Regeneration is the strategy to produce new cathode directly based on the spent one, Li source is required to compensate the Li loss, and thermal treatment is necessary to restore the former structure. Compared with recycling, regeneration has the advantage of fewer steps with higher utilization of valuable metals. However, it also suffers from several drawbacks, such as 1) impurities formed in spent cathode are hard to remove; 2) no general Li compensation level and calcination temperature, they are highly

sample dependent; 3) high energy consumption and strict experimental conditions. The most popular methods for regeneration are solid-state synthesis, hydrothermal treatment, Sol-Gel and co-precipitation, the advantage and disadvantage of each method are organized in the paper. Currently, most regenerations are still limited to lab scale, a lot more research work should be done to achieve large scale applications.

As aforementioned, each strategy/method has its advantages and defects. By now, a single strategy/method cannot stand alone to achieve high reusing efficiency with low cost and large scale. It is necessary to combine different strategies/methods to find a new process to fit for the increasing demands of LIBs. A desired process should be simple, low-cost, low energy consumption, high material recovery rate and efficiency with high purity and high electrochemical performance. Environmental impact should also be taken into account when a new route is designed. There have been tremendous excellent papers published for LIB recycling including some review papers, due to time and our abilities, we cannot cite every paper, we sincerely apologize for missing the outstanding ones.

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